

The Effects of Molecular Configuration on the Hindered Transport of Macromolecules in Microporous Membranes

by

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Abstract

A theoretical and experimental investigation was conducted to study the effects of molecular configuration on the hindered transport of macromolecules in porous membranes. A hydrodynamic theory was developed for the diffusion and convection of linear, flexible macromolecules through cylindrical pores of molecular dimensions. To examine the effects of molecular configuration, the theoretical results were compared to those of a hydrodynamic theory for solid, spherical solutes. In an experimental program designed to complement the theoretical study, solute diffusion rates through membranes with a well-defined pore geometry were measured for a variety of macromolecules.

The hindered transport theory for linear macromolecules accounts for both steric and hydrodynamic restrictions to solute transport. The steric hindrance, or partitioning of macromolecules between bulk solution and the cylindrical pores, was studied using a Monte Carlo technique, modeling the macromolecules as a freely jointed chain. This approach yielded the detailed radial distribution of macromolecules within the pore. The results of the partitioning calculations demonstrated that the partition coefficient, or equilibrium pore-to-bulk concentration ratio, of a chain with finite segment length can be substantially higher than that of a chain with an infinite number of infinitesimally short segments but with the same radius of gyration. Moderate, attractive polymer-pore interactions were also shown to produce dramatic increases in the partition coefficients of freely jointed chains with segments of finite length. Using an analogy to heat conduction, analytical solutions for the partition coefficient with attractive polymer-pore interactions were obtained for chains consisting of an infinite number of infinitesimally short segments.

To determine the hydrodynamic resistance to solute motion, a random-coiling macromolecule was modeled as a porous body, whose average shape and solvent permeability distribution were affected by confinement in a pore. Predicted hydrodynamic resistances to solute motion for flexible macromolecules were comparable to those for solid spheres when the Stokes-Einstein radius of solute was less than half the pore radius. For larger Stokes-Einstein radii the hydrodynamic resistances to the motion of flexible macromolecules were smaller than those for solid spheres. However, the less favorable partitioning of random coils between pores and bulk solution leads to lower transport rates for coils than spheres, for the same Stokes-Einstein radius and external driving force. This conclusion holds true for both diffusion and convection, over a wide range of solute-to-pore size ratios.

In the experimental investigation, the effective diffusion coefficients of four water-soluble macromolecules were determined in track-etched membranes containing uniform cylindrical pores. For each macrosolute, the diffusion coefficient in the membrane decreased with increasing solute-to-pore size ratio (based on Stokes-Einstein radius). The effective diffusion coefficients of ficoll, a highly crosslinked polysaccharide were in excellent agreement with those predicted by the theory for solid, spherical solutes. Effective diffusion coefficients for linear polyethylene oxide (PEO) were between those predicted for a solid sphere and for a linear, flexible polymer. In contrast, linear polyvinyl-pyrrolidone (PVP) and nearly linear dextran diffused through the membranes more rapidly than predicted by either theory. The hindered diffusion behavior of the linear (or nearly linear) macromolecules is consistent with their relative behavior on size-exclusion chromatographic columns, and can be explained by moderate, attractive interactions between the polymer and pore walls. In addition the trends observed for the hindered diffusion to ficoll, PEO and PVP relative to dextran are identical to those observed for the filtration of these polymers across the glomerular capillary wall in the kidney. These observations suggest that the deviations of hindered diffusion rates from theoretical predictions are governed more by the energetics of rearranging water molecules, or some other non-specific mechanism, than by the specific chemical nature of the porous medium.

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